

DESCRIPTION

NIOBIUM CAPACITOR AND METHOD FOR MANUFACTURING THE SAME5 TECHNICAL FIELD

The present invention relates to a niobium capacitor and a method for manufacturing same.

BACKGROUND ART

10 Tantalum capacitors are representative electrolytic capacitors. Tantalum capacitors are manufactured using for instance the following method. First, a sintered body is formed out of tantalum powder, next, a dielectric layer consisting of Ta_2O_5 is formed by anodic oxidation upon this
15 sintered body. An electrolyte layer and an electrode (cathode) are further formed on this dielectric layer.

Tantalum possesses excellent capacitor properties. However, its mineral ore deposits are relatively scarce, which makes tantalum expensive and subject to considerable
20 price fluctuations. For these reasons, there are ongoing studies concerning the use of niobium (Nb), which is more abundant and therefore less expensive, as a constituent material in capacitor anodes.

Anodic oxidation is used for forming dielectric layers
25 (Nb_2O_5) in the manufacture of niobium capacitors. However, Nb_2O_5 is less stable than Ta_2O_5 and is relatively more prone to releasing oxygen (O^{2-}), whereby Nb_2O_5 is converted into NbO and/or NbO_2 . Also, the closer to the niobium sintered

body, the stronger the tendency of released oxygen to migrate towards the niobium sintered body. Thus, dielectric layers of tantalum oxide and niobium oxide exhibit the differences illustrated in FIG. 8A and 8B.

5 As shown in FIG. 8A, a dielectric layer DL of Ta_2O_5 formed on a tantalum sintered body has a substantially uniform oxygen concentration across the whole layer. On the other hand, as shown in FIG. 8B, the composition of a dielectric layer DL of Nb_2O_5 changes first to NbO_2 and then
10 to NbO in the direction towards the interface BS. In other words, the closer to the interface BS, the more the oxygen concentration drops.

 In general, niobium oxide is an insulator (dielectric) when the number of oxygen atoms bonded to one niobium atom
15 is large, and a conductor when that number is small. In the case of FIG. 8B, Nb_2O_5 is an insulator whereas NbO is a conductor (in a strict sense, therefore, the layer DL in the figure cannot entirely function as a dielectric layer).

 Conventional niobium electrolyte capacitors have the
20 following drawbacks. As mentioned above, niobium oxide is less stable than tantalum oxide. In conventional niobium electrolyte capacitors, therefore, heat during soldering and the influence of voltage applied during use result in a tendency toward oxygen concentration changes in the vicinity
25 of the interface. As a result, the thickness of the conductive layer (NbO) varies, which entails that the thickness of the portion acting as a dielectric in the layer DL also changes. Specifically, conventional niobium

electrolyte capacitors have a drawback in that thermal or electric influences cause a deviation from the default permittivity value, which precludes obtaining the desired capacitor characteristics (capacitance, leakage currents, etc.).

DISCLOSURE OF THE INVENTION

In light of the above considerations, an object of the present invention is to provide a niobium electrolyte capacitor that eliminates or reduces dielectric layer instability found in conventional art.

In a first aspect of the present invention, a niobium capacitor comprises an anode with niobium as its main component, and a dielectric layer formed on this anode. The junction region between the anode and the dielectric layer contains manganese.

The dielectric layer contains preferably Nb_2O_5 .

The anode has preferably a surface layer with interstitial niobium oxide or interstitial niobium nitride as its main component.

The anode is preferably a porous sintered body of a compressed niobium-containing powder.

The niobium-containing powder has preferably a surface layer containing manganese.

The junction region contains preferably NbO and Mn .

The junction region contains preferably MnO_2 .

The junction region contains preferably 0.1 to 10wt% of manganese.

The dielectric layer is preferably formed by anodic oxidation on the anode, and the junction region contains preferably 0.1 to 3wt% of manganese.

5 In the constitution of the niobium capacitor according to the present invention there is further provided a solid electrolyte layer formed on the dielectric layer. This solid electrolyte layer consists of MnO_2 .

In a second aspect of the present invention is provided a method for manufacturing a niobium capacitor.
10 This method comprises the steps of forming an anode containing niobium and manganese, and of forming a dielectric layer on the anode.

The step of forming the anode involves preferably forming a compressed molded product made of a niobium-
15 containing powder containing in the surface layer thereof 0.1 to 10wt% of manganese. The compressed molded product is then subsequently sintered.

The step of forming the anode involves preferably forming a sintered body made of niobium-containing powder,
20 and then doping the sintered body with manganese.

In a third aspect of the present invention is provided another method for manufacturing a niobium capacitor. This method comprises the steps of forming an anode containing niobium, and of forming a dielectric layer containing
25 niobium oxide as its main component and 0.1 to 10wt% of manganese.

In the step of forming a dielectric layer, the anode undergoes anodic oxidation using preferably a chemical

conversion solution containing manganese ions. Alternatively, in the step of forming a dielectric layer, the anode is oxidized in a vapor-phase atmosphere containing manganese.

The anode preferably contains any one of niobium,
5 niobium oxide and niobium nitride, as its main component.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing the structure of a niobium electrolyte capacitor according to the present
10 invention.

FIG. 2 is a perspective view of thin-layer capacitors used to verify the effect of the present invention.

FIG. 3 is a cross-section of FIG. 2 along the line III-III.

15 FIG. 4 is a graph showing the "DC bias voltage (V) - capacitance change rate (%)" relationship for the capacitors of FIG. 2.

FIG. 5 shows the measurement results for leakage currents in the capacitors of FIG. 2.

20 FIG. 6 is a graph showing the relationship between manganese concentration and capacitance change rate.

FIG. 7 is a graph showing the relationship between applied voltage and capacitor capacitance.

FIG. 8A is a schematic diagram showing the
25 constitution of a dielectric layer in a tantalum capacitor.

FIG. 8B is a schematic diagram showing the constitution of a dielectric layer in a niobium capacitor.

BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention are described in detail below, with reference made to relevant accompanying drawings.

5 As shown in FIG. 1, the niobium electrolytic capacitor according to the present invention comprises a porous anode 1 consisting essentially of sintered niobium powder, an anode rod 2 partly buried in the anode 1, and a cathode layer 3. Specifically, there are formed a dielectric layer 4
10 and a solid electrolyte layer 5 between the anode 1 and the cathode layer 3. The dielectric layer 4 is in close contact with the anode 1, in such a way so as to prevent an electric connection between the anode 1 and the solid electrolyte layer 5.

15 The anode 1 can be formed by sintering a compression-molded niobium-containing powder. Niobium powders that may be used have a specific surface area (weight ratio capacitance) of 2000 CV/g or more (preferably 2000 to 500000 CV/g or more). The sintering temperature is set, for
20 instance, from 1000 to 1500°C.

In the embodiment shown in the figure, niobium is the main component of the anode 1, but the present invention is not limited thereto. The main component may also be, besides niobium, a niobium oxide or a niobium nitride. Niobium oxide
25 and niobium nitride need not be homogeneously distributed throughout the sintered body and may be present only at the surface. A typical niobium oxide is NbO, while a typical niobium nitride is NbN. The niobium oxide or niobium nitride

is preferably interstitial. The dielectric layer 4, as shown in FIG. 8B, contains a niobium oxide such as Nb_2O_5 , etc. The solid electrolyte layer 5 consists, for instance, of MnO_2 . Alternatively, the solid electrolyte layer 5 may consist of a conductive polymer. Conductive polymers include for instance polythiophenes or polypyrroles.

In the present invention, the "junction region" between the anode 1 and the dielectric layer 4 contains manganese (Mn). The "junction region" refers herein to a region encompassing the boundary between the anode 1 and the dielectric layer 4, and adjacent areas to this boundary. The junction region contains manganese preferably in the form of manganese dioxide MnO_2 . As a boundary, the junction region may be considered to be divided into a sintered body portion and a dielectric layer portion. There are three ways in which manganese may be contained in the "junction region", as follows. (1) Manganese is contained only in the sintered body portion. (2) Manganese is contained only in the dielectric layer portion. (3) Manganese is contained both in the sintered body portion and in the dielectric layer portion.

The amount of manganese in the aforementioned junction region is for instance 0.1wt% or more. With an amount of manganese below 0.1wt%, niobium oxide tend to become unstable, as in conventional cases. The upper limit of manganese content depends on the way the dielectric layer 4 is formed, of which two concrete examples are described next. In the first example, the dielectric layer 4 is formed by

anodic oxidation using a chemical conversion solution containing manganese ions. In this case, the manganese content in the dielectric layer is preferably 3wt% or less. The reason for this is that an amount of manganese above 3wt% results in manganese salts leaching towards the surface of the dielectric layer 4, which prevents the formation of a dielectric layer 4 having a suitable, intimate adhesion to the anode 1. The second example involves the formation of the dielectric layer 4 by vapor-phase oxidation in an atmosphere containing manganese. In this case, the amount of manganese is 10wt% or less. This limiting figure derives from the fact that the upper limit of manganese content in vapor-phase oxidation stands ordinarily at about 10wt%. If feasible, therefore, the manganese content may be greater than 10wt%.

Two techniques may be devised for incorporating Mn into the anode 1. In a first technique, the anode 1 is formed using a niobium powder containing Mn in its surface. In a second technique, a niobium powder not containing Mn is compression-molded and then sintered. The molded product is subsequently doped with Mn. The amount of Mn in the sintered body (value before formation of the dielectric layer 4) is set in accordance with the Mn content that will be required at the junction region, and is for instance 0.1 to 10wt%.

In the formation of the dielectric layer 4 by anodic oxidation, a 0.1wt% aqueous solution of phosphoric acid is used for instance as the chemical conversion solution. If Mn ions are present in the chemical conversion solution, the

dielectric layer will contain Mn when formed. Anodic oxidation is carried out by applying a predetermined voltage between the sintered body, dipped in the chemical conversion solution, and the cathode that will be paired with this
5 sintered body. The temperature of the chemical conversion solution, ranges from room temperature to 100°C. The applied voltage (target voltage) ranges from 5 to 120 V, and the current density ranges from 10 to 100 $\mu\text{A}/\text{cm}^2$. The current-application time ranges from 0.1 to 30 hours. Current is
10 preferably applied under small current values in order to keep leakage currents low.

Vapor-phase oxidation may be carried out by heating the anode 1 in a normal air atmosphere. The heating of the anode 1 may alternatively take place at reduced pressure or
15 in an atmosphere of oxygen diluted in argon, etc. The heating temperature ranges for instance from 200 to 400°C. The atmosphere may contain Mn during vapor-phase oxidation. That way, the formed dielectric layer ends up containing Mn.

Niobium oxides are unstable in conventional niobium
20 capacitors, so the characteristics of the capacitor vary in accordance with the influence of heat or applied voltages. This problem can be effectively suppressed or reduced through a "junction region" containing manganese. The presence of manganese keeps constant the number of oxygen
25 atoms bonded to niobium in the dielectric layer 4, thereby stabilizing niobium oxide. For instance, oxygen from MnO_2 replenishes oxygen released by niobium oxide, wherein the amount of oxygen supplied depends on the amount released. As

a result, the number of oxygen atoms bonded to niobium is kept constant. The presence of Mn in the vicinity ("junction region") of the interface where a niobium valence change is likely to occur results as well in niobium oxide becoming
5 more stable than in conventional cases.

In order to verify the effect of the present invention, experiments were carried out using the thin-layer capacitors X1 and X2 shown in FIG. 2 and 3.

The capacitors X1 and X2 are formed on an ordinary
10 glass substrate 10. As can be seen in FIG. 2, the glass substrate 10 supports conductors 20A, 20B having an identical shape. The conductors 20A, 20B were formed by DC sputtering (the thickness of the conductors was about 300 nm, and their projected areas were 1 cm²). Pure niobium and
15 manganese were mixed in vapor phase for forming the conductor 20A by sputtering. The obtained conductor 20A contained 6wt% of manganese and 94wt% of niobium. The conductor 20B was formed with niobium alone.

Dielectric layers 30A and 30B were formed respectively
20 over the conductors 20A and 20B (FIG. 2). The dielectric layers 30A and 30B were formed by anodic oxidation using a 0.1wt% solution of phosphoric acid. The final voltage FV herein was 25.5V and the treatment lasted 2 hours.

The dielectric layers 30A and 30B were covered by an
25 electrolyte 40. The electrolyte used was a 0.1wt% solution of phosphoric acid.

FIG. 4 is a graph showing the "DC bias voltage (V) - capacitance change rate (%)" relationship for capacitors X1

and X2. The measurements were carried out by contacting an electrode rod 50 with the conductor 20A (20B), and an electrode rod 51 with the electrolyte 40, as shown in FIG. 3. In this state, a predetermined voltage was applied to capacitors X1 and X2 in order to measure their capacitances. The graph in FIG. 4 shows the capacitance changes for each of the applied voltages relative to a baseline capacitance corresponding to an applied voltage of 1.5V.

As the graph in FIG. 4 shows, the capacitor X2 (where pure niobium was used as the conductor 20B) displays a highly voltage-dependent capacitance, i.e. large capacitance changes in response to voltage changes. By contrast, hardly any capacity changes were observed for the capacitor X1 (where the conductor 20A contained Mn). That is, voltage dependency was lower.

FIG. 5 shows the measurement results for leakage currents in the capacitors X1 and X2. These leakage currents are values measured after 1 minute of applying a voltage equivalent to 65% of the aforementioned FV voltage (25.5V) (the measurements were performed for 10 samples each of the capacitors X1 and X2). As can be seen in FIG. 5, leakage currents were markedly lower for capacitor X1, as compared with capacitor X2.

The relationship between manganese concentration in the dielectric layer of the niobium capacitor and the characteristics of the capacitor is explained next, with reference made to FIG. 6 and 7. Capacitors with a constitution identical to that of capacitors of FIG. 2 and 3

were used for studying this relationship. The conductive layer formed by pure niobium had a diameter of 1cm. Four types of conductive layer with differing manganese concentrations were prepared (0wt%, 0.1wt%, 0.2wt%, 2.0wt%).

5 A 0.1wt% phosphoric acid solution containing the target amount of Mn ions was used as the chemical conversion solution. The final voltage FV herein was 20V and voltage was applied for 2 hours.

The graph in FIG. 6 shows the capacitance change rate

10 when the voltage applied to the capacitors changed from 0V to 3V. The graph in FIG. 7 illustrates the relationship between applied voltage and capacitance for the different manganese concentrations (0.1wt%, 0.2wt%, 2.0wt%). As these graphs show, the rate of capacitance change becomes smaller

15 (capacitance stabilization) as the manganese concentration increases. This effect can be satisfactorily achieved even for concentrations of manganese of 0.1wt%.

As will be apparent to those skilled in the art, the embodiments of the present invention described above can be

20 subject to all manner of modifications. It is therefore to be understood that such modifications may be made and other arrangements may be devised by those skilled in the art without departing from the spirit and the scope of the present invention as defined by the appended claims.